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ABLATIVE AND INSULATING PROPERTIES OF OUTGASSED BORON NITRIDE AND BORON NITRIDE COMPOSITE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

[Hot-pressed boron nitride that had been outgassed in vacuum ablated with negligible spalling when exposed to a jet of arc-heated air.] The measured heats of ablation ranged from 30 to 35 MJ/kg for an enthalpy potential range of 16 to 23 MJ/kg. No ablation occurred in nitrogen at enthalpies up to 26 MJ/kg.

[A composite of boron nitride and phenolic resin, produced in an attempt to reduce thermal conductivity, was evaluated in both arc-heated air and nitrogen at enthalpy potentials from 8 to 15 MJ/kg and from 15 to 21 MJ/kg, respectively. Poor high-temperature bonding characteristics reduced the heats of ablation to approximately half those of hot-pressed boron nitride.]

The insulation efficiencies of the composite, pyrolytic boron nitride, boron nitride, and phenolic nylon, were studied [at cold-wall convective heating rates of 1.4 to 2 MJ/m²-sec in arc-heated air and 1.9 to 2.5 MJ/m²-sec in arc-heated nitrogen. (When compared on the basis of the total cold-wall heat input per initial pound of material for a back-face temperature rise of 167° K, the composite was twice as effective as either pyrolytic boron nitride or hot-pressed boron nitride.)]

INTRODUCTION

Boron nitride has many properties that make it desirable as a heat-shield material on spacecraft. Its sublimation temperature is nearly as high as those of the carbon materials, which have been extensively investigated (ref. 1); whereas its oxidation rate is much less. Other desirable properties include good strength at high temperature and excellent machinability (ref. 2). Bro and Steinberg (ref. 3) conducted ablation tests on boron nitride. They reported that even in a nonreactive gas (nitrogen), considerable material loss resulted from surface spalling so that boron nitride was of little value as an ablation material. However, Carter and Sabol (ref. 4) found that applying heat to boron nitride before testing reduced spalling, and they concluded that the improved performance was attributable to expulsion of residual water from the boron nitride. In an unpublished study, Mr. R. Griffin at Ames Research Center found that preconditioning in a vacuum environment would also eliminate the spalling of boron nitride, undoubtedly as a result of the removal of residual water. Thus, because space vehicles normally exist in a vacuum

environment prior to being exposed to reentry heating, a boron-nitride heat shield would not be expected to spall significantly. For this reason, it appeared desirable to evaluate outgassed boron nitride for heat of ablation and insulation efficiency.

Because boron nitride has an undesirably high thermal conductivity, a composite of boron nitride and phenolic resin was fabricated in an attempt to reduce thermal conductivity, and the heat of ablation and insulation efficiency were determined. In addition, the insulation efficiencies of pyrolytic boron nitride and phenolic nylon were evaluated.

SYMBOLS

H_{ts}	test stream enthalpy
H_w	wall enthalpy of ablator
\dot{m}	mass loss rate
Q	total cold-wall heat input, $\dot{q}(t_{\Delta T=167^\circ K})$
Q^*	effective heat of ablation, \dot{q}_0/\dot{m}
\dot{q}	cold-wall convective-heat-transfer rate
\dot{q}_0	hot-wall convective-heat-transfer rate in the absence of ablation
T	temperature
$t_{\Delta T=167^\circ K}$	time for temperature rise of $167^\circ K$
W	initial weight per unit area

EXPERIMENT

Facility

The ablation materials were exposed to the high-energy, low-density stream generated by an arc-jet wind tunnel described in detail in reference 5. The high-energy, partially dissociated gas expands from a plenum chamber through one of the available conical nozzles and discharges into a vacuum chamber as a free jet of either 0.030-m diameter at $M = 3.7$ or 0.038-m diameter at $M = 4.2$. The nominal test conditions are listed in table I. The test-stream energy was varied from 8 to 25 MJ/kg by changing the electrical input energy.

Material Samples and Test Conditions

The material samples tested and the conditions under which they were run are summarized in table II. As is shown in the table, insulation efficiency of all materials was tested both in air and in nitrogen with the $M = 4.2$ nozzle. The ablation tests on the boron nitride-phenolic resin composite were also performed in both air and nitrogen, using the $M = 4.2$ nozzle. Prior to the ablation tests of the hot-pressed boron nitride, however, the $M = 3.7$ nozzle was installed to achieve a greater stream energy.

Ablation test specimens.- The hot-pressed boron nitride specimens were axisymmetric 0.00952-m-diameter cylinders, 0.0444 m long, with a nose radius of 0.0254 m. The boron nitride-phenolic resin composite test sample was a 0.00318-m-diameter cylinder pressed into the 0.00952-m-diameter concentric main body before the 0.0254-m nose radius was turned. The samples were a mixture of 50-percent boron nitride powder and 50-percent phenolic resin by weight compressed to a density of 1554 kg/m³ and baked. A typical ablation test body is shown in figure 1.

Insulation efficiency specimens.- The insulation efficiency sample was a 0.00318-m-diameter cylinder of hot-pressed boron nitride, pyrolytic boron nitride (low conductivity in the axial direction), boron nitride-phenolic resin composite, or phenolic nylon (1184 kg/m³). The sample lengths, l , were adjusted to maintain a constant weight-to-area ratio of 13.96 kg/m². The samples were supported in 0.0095-m-diameter axisymmetric body with a nose radius of 0.0254 m. The body material was the same as that of the specimen, namely, either hot-pressed boron nitride, composite, or phenolic nylon. A typical insulation efficiency test body is shown in figure 2.

Test Procedure and Measurements

Ablation tests.- The noses of the ablation test bodies were located on the axis of the test stream 0.0127 m and 0.0254 m downstream of the 0.030-m and 0.038-m-diameter nozzle exit planes, respectively. A shield in front of the model prevented exposure during the initiation period. When steady flow was established, the shield was removed to expose the test body to the heated gas for a predetermined time. To determine mass loss, the material samples were weighed on an analytical balance before and after the tests to an accuracy of ± 0.5 mg. The boron nitride bodies were preconditioned by baking at 1090° K for 8 hours and then were placed in a vacuum for at least 24 hours prior to testing. They were stored in a closed, desiccated metal container until tested.

Insulation efficiency tests.- The noses of the insulation test bodies were located on the stream axis 0.0254 m downstream of the 0.038-m-diameter nozzle exit plane. The shield was removed after the flow conditions became steady. When the temperature of the rear surface exceeded 167° K, the test was terminated. The temperature-time history of each sample was measured with a chromel-alumel thermocouple (0.00013-m diameter) cemented in an indentation on the rear surface.

Heating rates.- Cold-wall convective heating rates were measured by the transient heat-transfer probe shown in figure 3. The probe was a 0.00318-m-diameter copper cylinder radially supported in a stainless steel body by three 0.00013-m-diameter wires to minimize conduction losses. A chromel-alumel thermocouple spot-welded to the rear face of the copper slug was used to measure the temperature rise of the copper with time. The heating rate in the absence of ablation was calculated from the initial slope of the temperature versus time curve, the mass, surface area, and specific heat of the copper slug. Measurements of the stagnation-point heating rate are plotted in figure 4 as a function of test-stream energy.

Surface temperature measurements.- A total-radiation pyrometer mounted inside the tunnel was used to measure the surface temperature of each ablation specimen during exposure. In reducing the pyrometer measurement to temperature a constant emissivity factor was applied for each material. The values of emissivity used were as follows: pyrolytic boron nitride, 0.8 (ref. 6); boron nitride, 0.81 (ref. 7); phenolic nylon, 0.83 (ref. 8); and composite 0.82 (arithmetic average of boron nitride and phenolic nylon).

RESULTS AND DISCUSSION

Effective Heats of Ablation

Hot-pressed boron nitride.- Boron nitride samples exposed to a nitrogen stream and a maximum heating rate of $3.7 \text{ MJ/m}^2\text{-sec}$ experienced no weight loss. Although the observed surface temperature was 1530°K , calculations using Clapeyron's equation show that for the test pressure range of 0.08 to 0.10 atm, the sublimation temperature is 2410° to 2450°K . For this calculation, Clapeyron's equation was normalized using a sublimation temperature of 2973°K at 1 atm (ref. 2).

When the boron nitride samples were exposed to an air stream, the reduction in mass, with negligible spalling, progressed approximately linearly with exposure time. The measured mass loss is plotted as a function of time for three values of stream centerline energy in figure 5. To minimize initial transient effects, the mass loss per unit time was obtained from the slope of the straight line faired through the data at each energy level.

The mass loss rate per unit area as a function of enthalpy potential in air is shown as circled points in figure 6. The solid line in the same figure is the theoretical mass loss rate per unit area due to surface combustion for boron nitride calculated by Dennison and Dooley (ref. 9), and the dashed line is the more complete analysis of Bowen and Gorton (ref. 10). The experimental mass loss rate per unit area is about 2.3 times the mass loss rate per unit area calculated for surface combustion, indicating that sublimation and possibly gas-phase combustion also occurred. This conclusion is substantiated by the observed surface temperature range of 2270° to 2510°K that covers the calculated range for the sublimation temperature.

The experimentally determined effective heat of ablation, Q^* , is shown as circled points in figure 7. For comparison, the theoretical values of Q^* , (ref. 9) for surface combustion, gas-phase combustion, and surface and gas-phase combustion are shown as solid lines.

From comparison of the curves, it is evident that when gas-phase combustion occurs Q^* is greatly reduced from that of surface combustion; at an enthalpy potential of 21 MJ/kg, the predicted reduction in Q^* is 57 percent. The experimental data lie between the theoretical gas-phase combustion and surface and gas-phase-combustion curves. This would indicate that surface combustion and gas-phase combustion occurred simultaneously.

Boron nitride-phenolic resin composite.- Composite models were exposed to nitrogen and air streams (fig. 8). The reduction in mass with exposure time at various center-line energies in nitrogen and air is shown in figures 9(a) and 9(b), respectively. The mass loss rate used to determine Q^* was obtained from the slope of the straight line faired through the data at each energy level.

The variation of Q^* with enthalpy for boron nitride, the boron nitride-phenolic resin composite, and phenolic nylon (ref. 11) is shown in figure 10. For boron nitride in air, Q^* is at least a factor of 2 higher than Q^* for either the composite or the phenolic nylon. For the composite in air at an enthalpy potential of 15 MJ/kg Q^* is 18.5 percent lower than that of phenolic nylon. This result was disappointing because the purpose of the composite was to utilize the high Q^* of the boron nitride. The result may be explained by the fact that the boron nitride-phenolic resin composite was a mechanical rather than a chemical bond and therefore the phenolic resin decomposed, releasing the entrapped BN particles before the full advantage of the high heat of vaporization of boron nitride could be realized. It is noted that at an enthalpy potential of 15 MJ/kg the Q^* of the composite in air is 32 percent lower than that in nitrogen. This decrease in Q^* is attributed to combustion of the composite in air. It is readily seen that Q^* of the composite is about one third that of the boron nitride at an enthalpy potential of 15 MJ/kg.

Measurement of the Insulation Efficiency

Four materials - boron nitride-phenolic resin composite, pyrolytic boron nitride, hot-pressed boron nitride, and phenolic nylon - were evaluated in terms of the insulation efficiency,

$$\frac{Q}{W} = \frac{\dot{q} \Delta T = 167^\circ \text{K}}{W}$$

The reasons for selecting this parameter and the 167° K back-face temperature rise limit have been discussed in reference 12. The measured insulation efficiencies are plotted as a function of cold-wall convective-heat-transfer rate, q , in figure 11. The insulation efficiency of the composite in air and nitrogen is only about 20 percent of that of phenolic nylon, but is

about twice that of either pyrolytic or hot-pressed boron nitride. The insulation efficiencies of pyrolytic boron nitride are about 25 and 10 percent greater than that of boron nitride in air and nitrogen, respectively. All the materials, except boron nitride, were less efficient in air than in nitrogen. The lower efficiency was due to the additional heat generated by combustion in the air tests. No difference was observed between the efficiency of the boron nitride in air and nitrogen because the surface did not have sufficient time to reach combustion temperature since the back-face temperature rise was extremely rapid. The maximum observed surface temperature in air was 1000°K , and this was below 1123°K (ref. 2), the combustion temperature of pyrolytic boron nitride in a 0.33 m/sec air stream at 1 atm.

CONCLUDING REMARKS

Hot-pressed boron nitride ablated in air with negligible spalling when the absorbed water was removed by application of heat and vacuum prior to testing. Boron nitride has a measured heat of ablation of about 35 MJ/kg at an enthalpy potential of 21 MJ/kg. Comparison with theory and with tests in nitrogen gas showed that gas phase as well as surface combustion occurred during exposure to air.

The effective heat of ablation of a boron nitride-phenolic resin composite at an enthalpy potential of 15 MJ/kg was 15.7 MJ/kg in nitrogen and 10.5 MJ/kg in air. The lower heat of ablation in air is attributed to gas-phase combustion of the composite in air.

The insulation efficiency of the boron nitride-phenolic resin composite was only about 20 percent that of phenolic nylon, but was twice that of either pyrolytic boron nitride or hot-pressed boron nitride. The insulation efficiency of the three materials was lower in air than in nitrogen. This is explained by the additional heat caused by exothermic combustion in the air tests. Boron nitride showed no difference between insulation efficiency in air and in nitrogen because the surface temperature was too low for combustion to occur.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif., July 25, 1966
129-01-09-06

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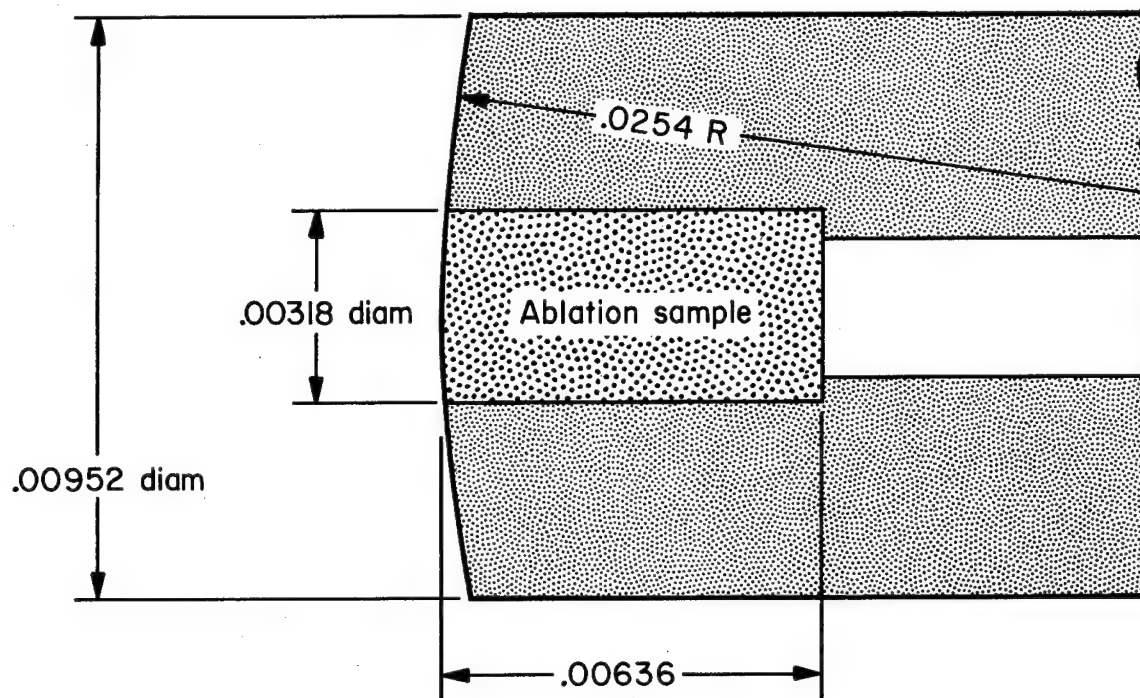
TABLE I - TEST CONDITIONS

Nozzle diameter, m	Test gas	Test gas flow rate, gm/sec	Plenum chamber pressure, atm	Test chamber pressure, atm	Impact pressure, atm	Mach number
.030	N ₂	2.269	.60-.69	.00132	.07-.09	3.7
.030	Air	2.269	.65-.75	.00132	.08-.10	3.7
.038	N ₂	2.269	.45-.49	.00114	.08-.09	4.2
.038	Air	2.269	.45-.50	.00114	.08-.10	4.2

TABLE II - TEST MATERIALS

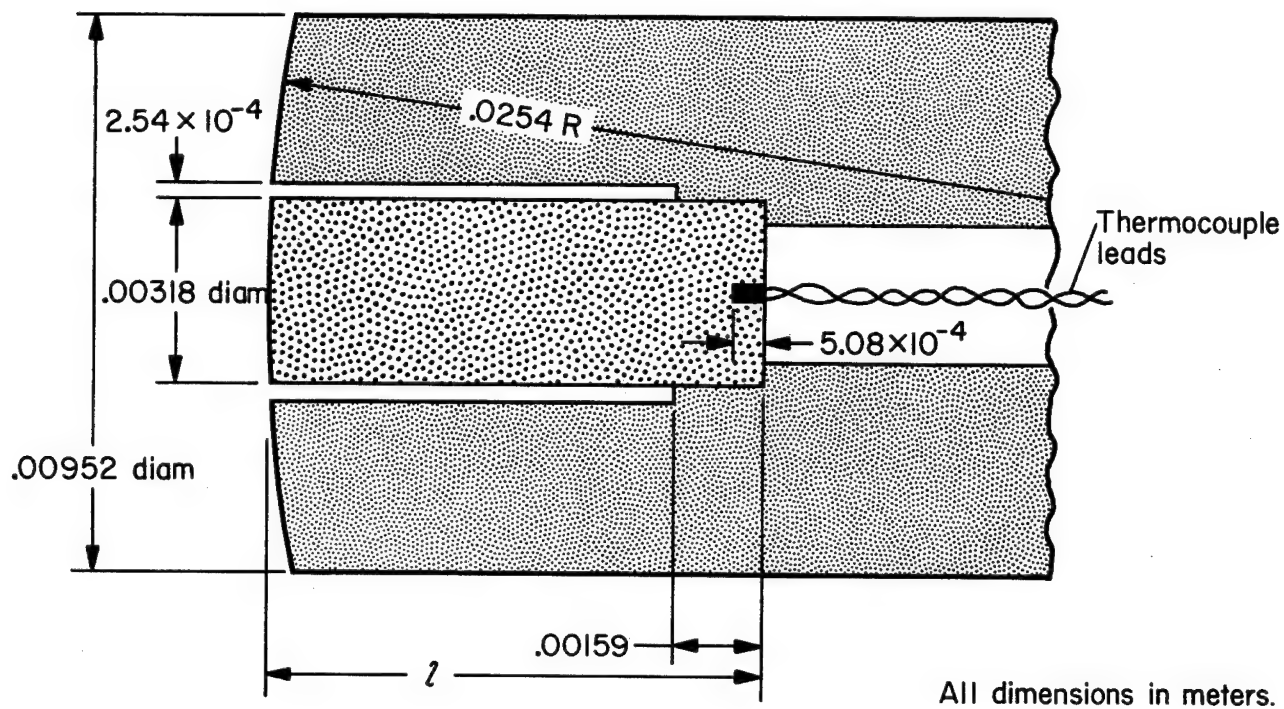
Materials	Ablation test			Insulation efficiency test		
	Test gas		Nozzle diameter, m	Test gas		Nozzle diameter, m
	Air	N ₂		Air	N ₂	
BN	X	X	.030	X	X	.038
Composite	X	X	.038	X	X	.038
PBN				X	X	.038
PN				X	X	.038

BN Boron nitride
 Composite 50% boron nitride-50% phenolic resin
 PBN Pyrolytic boron nitride
 PN Phenolic nylon



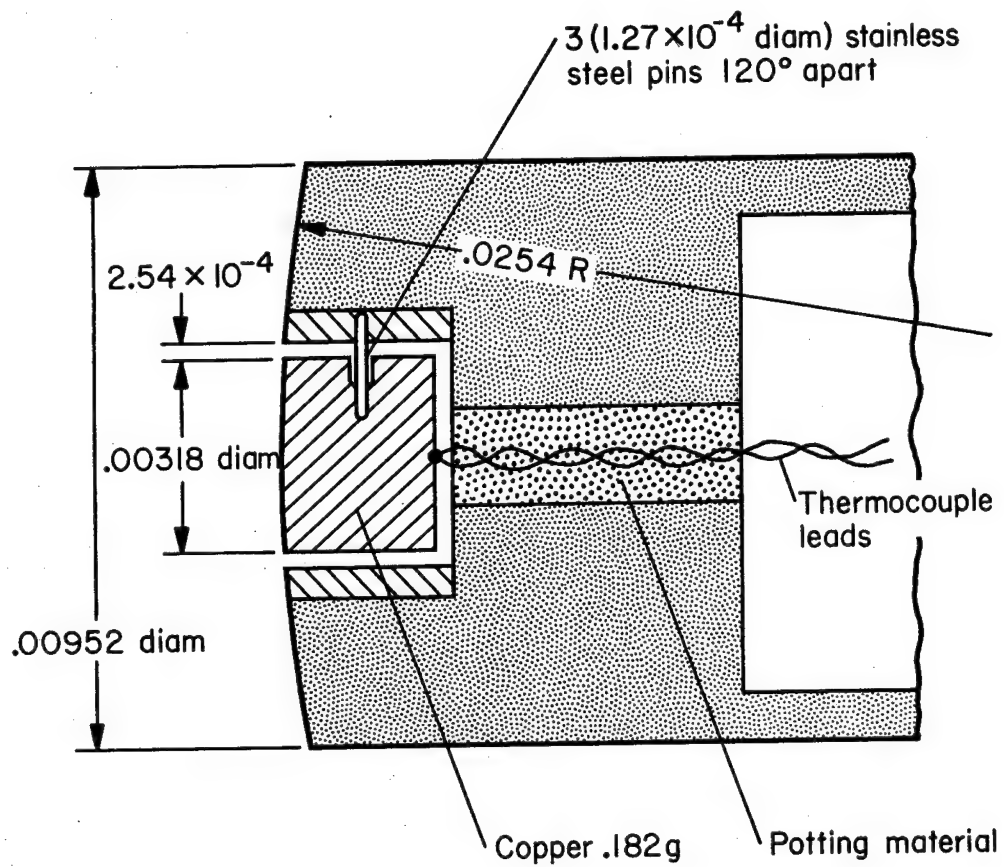
All dimensions in meters.

Figure 1.- Ablation test body.



Body material	Test material	l
Composite	Composite	8.96×10^{-3}
Boron nitride	Pyrolytic boron nitride	6.35×10^{-3}
Boron nitride	Boron nitride	6.35×10^{-3}
Phenolic nylon	Phenolic nylon	11.80×10^{-3}

Figure 2.- Insulation efficiency test body.



All dimensions in meters.

Figure 3.- Heat-transfer probe.

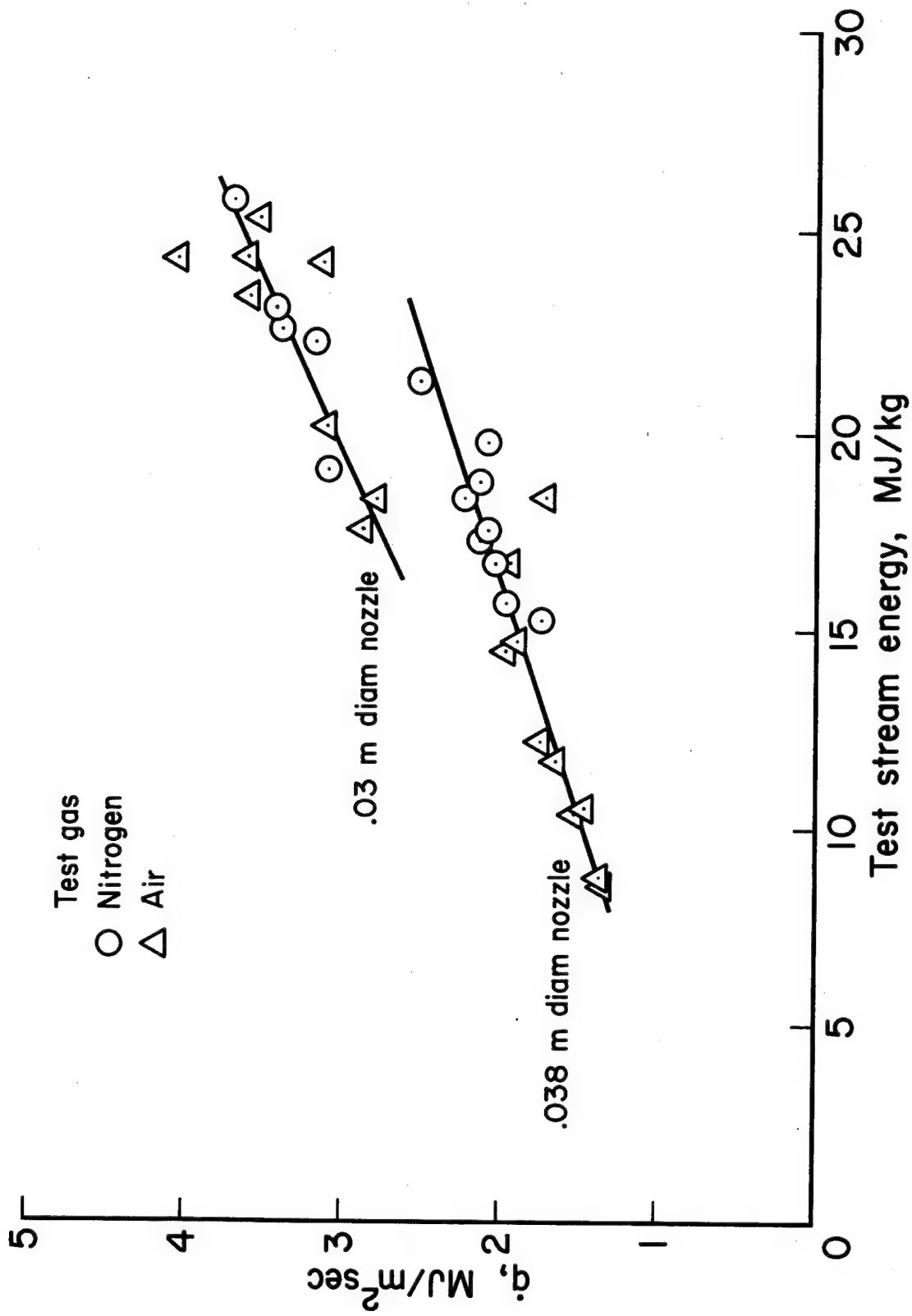


Figure 4.- Variation of stagnation region heat-transfer rate with test-stream energy.

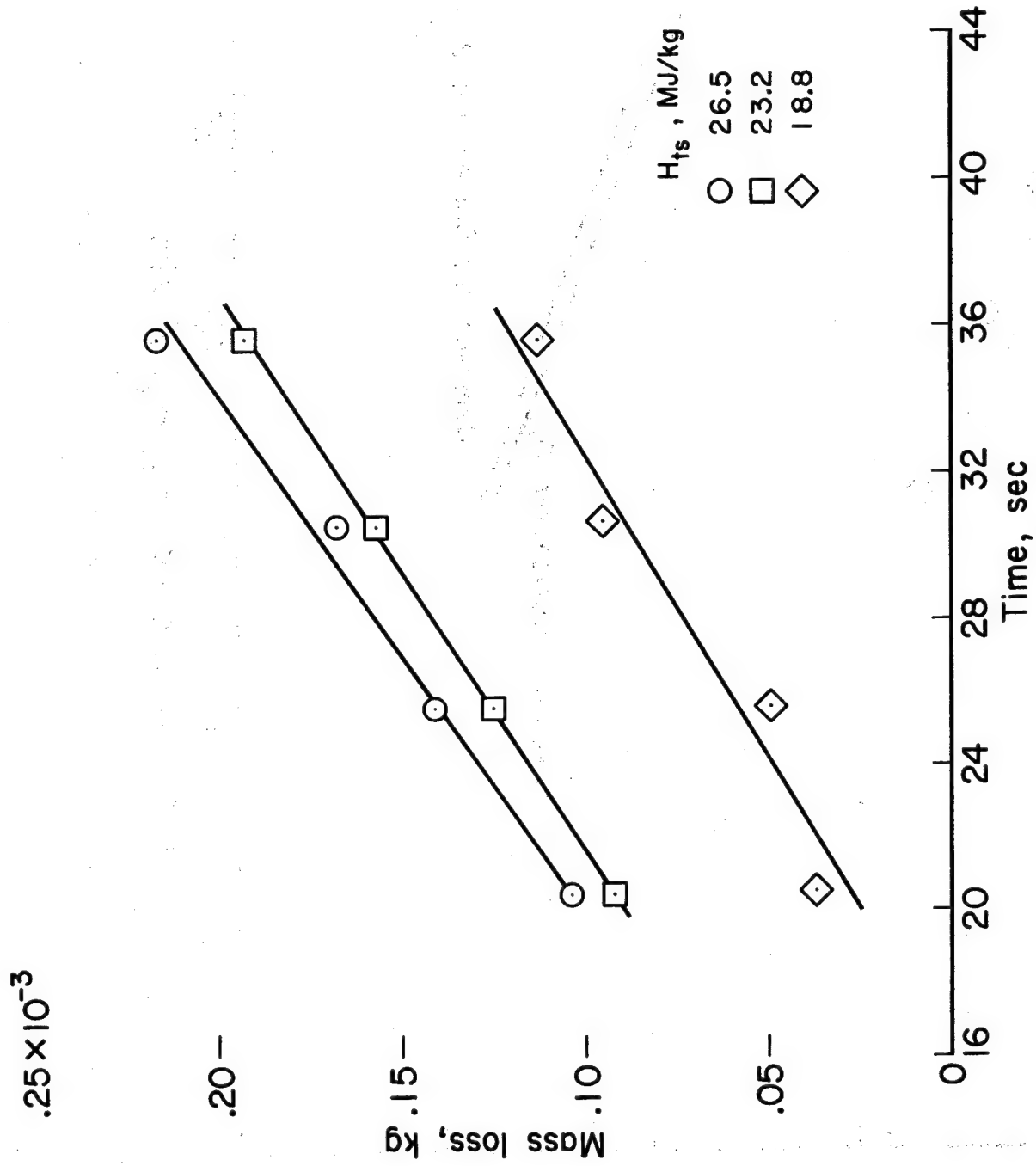


Figure 5.- Hot-pressed boron nitride weight loss in air.

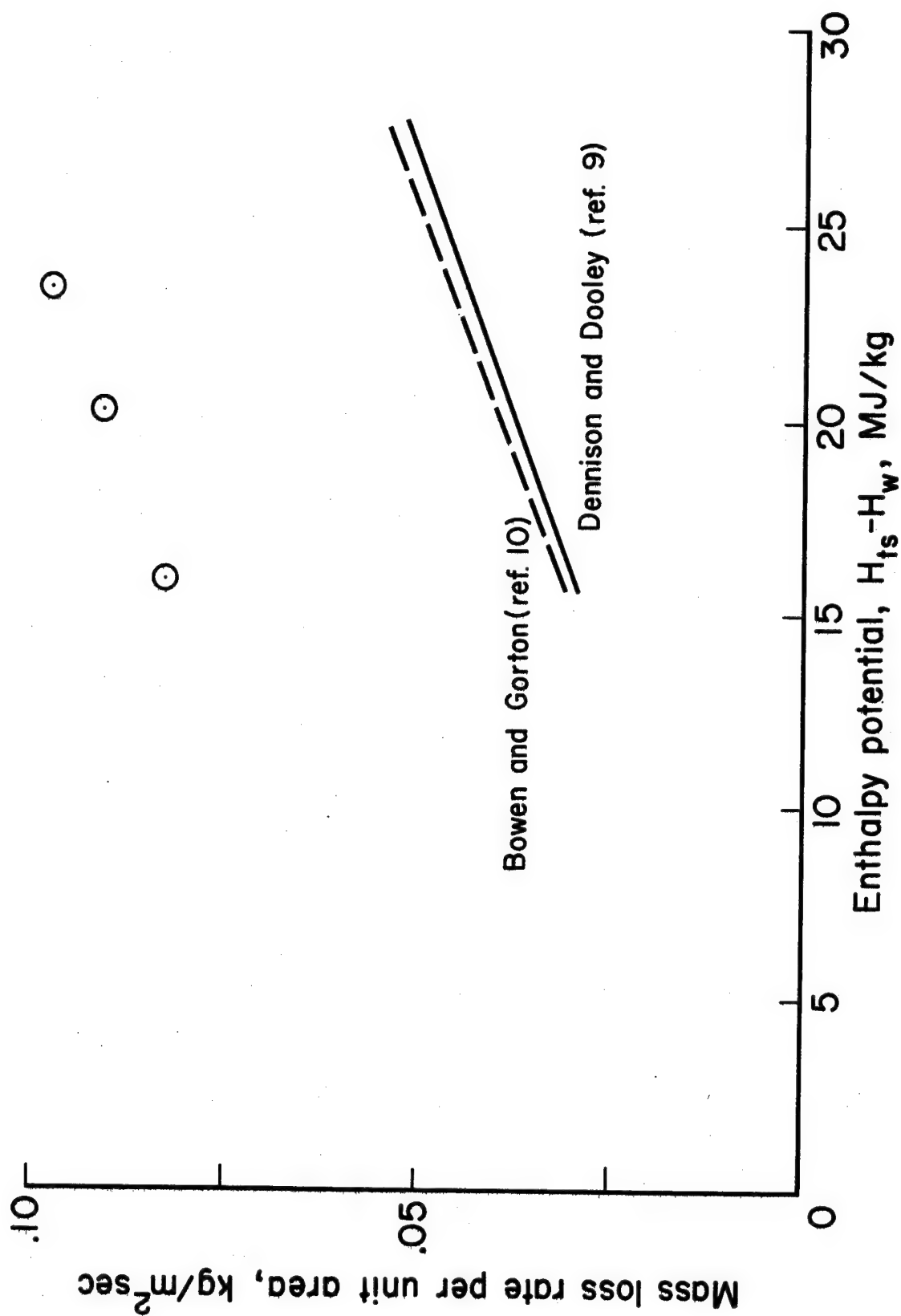


Figure 6.- Mass loss rate per unit area for hot-pressed boron nitride in air.

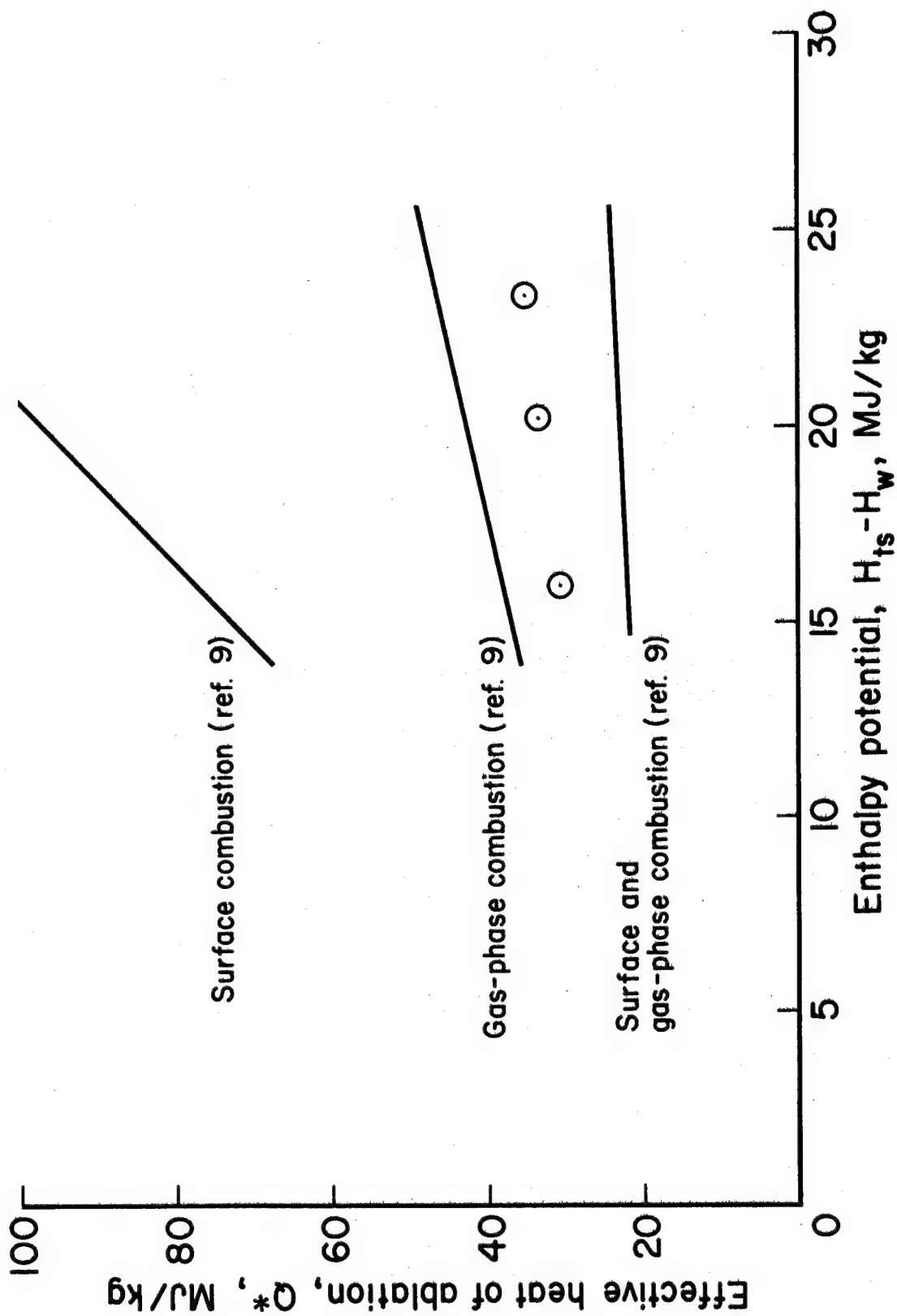


Figure 7.- Effective heat of ablation of hot-pressed boron nitride in air.

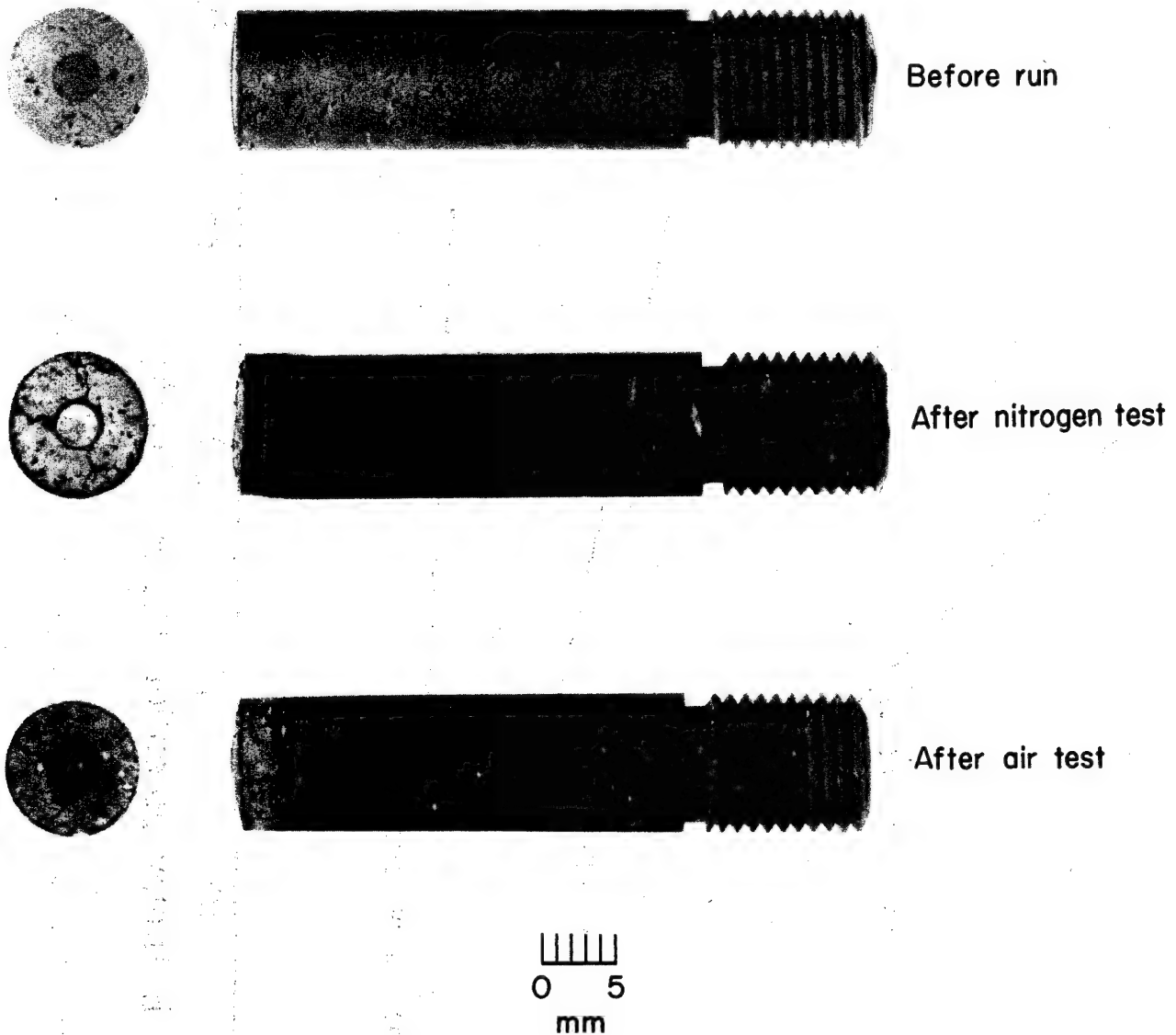
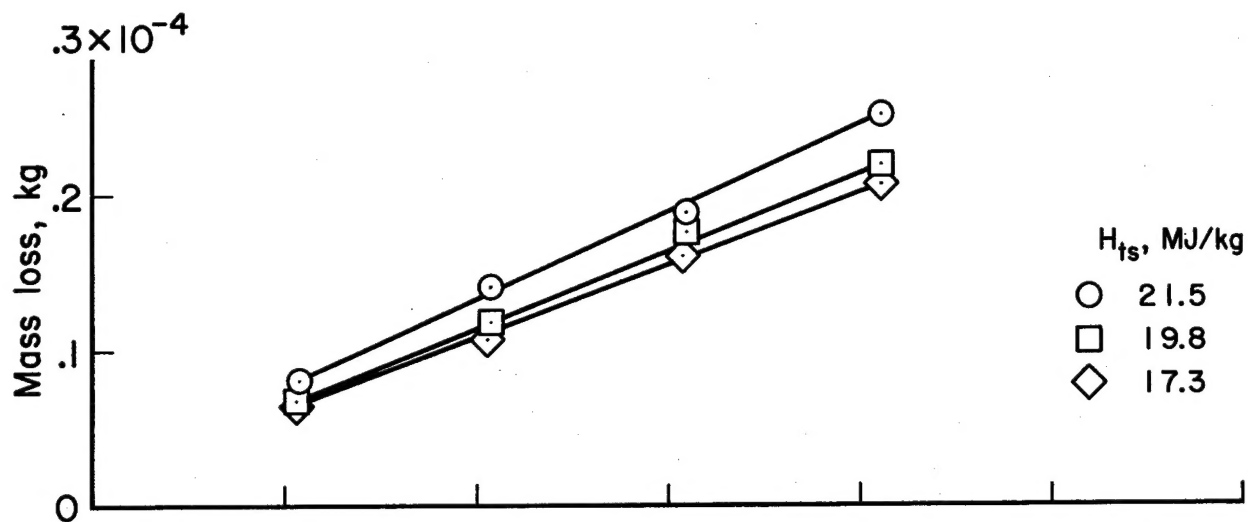
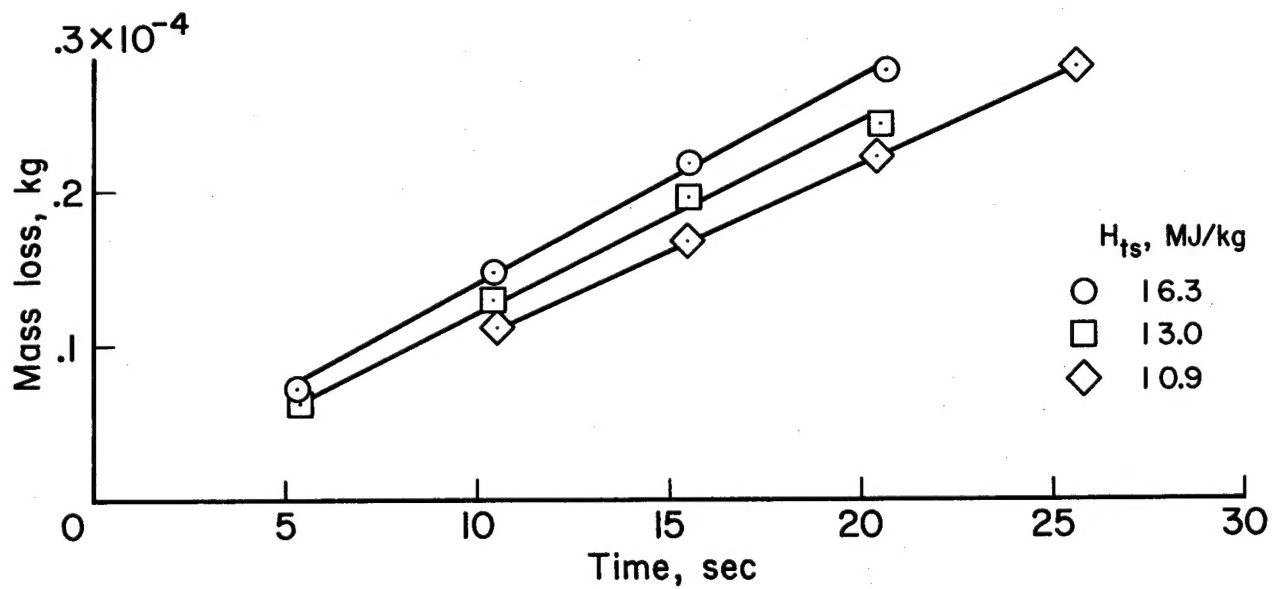


Figure 8.- Appearance of composite model before and after testing in nitrogen and air at test-stream energy of 16×10^6 J/kg and $t = 20.5$ sec.



(a) Nitrogen.



(b) Air.

Figure 9.- Boron nitride-phenolic resin composite weight loss.

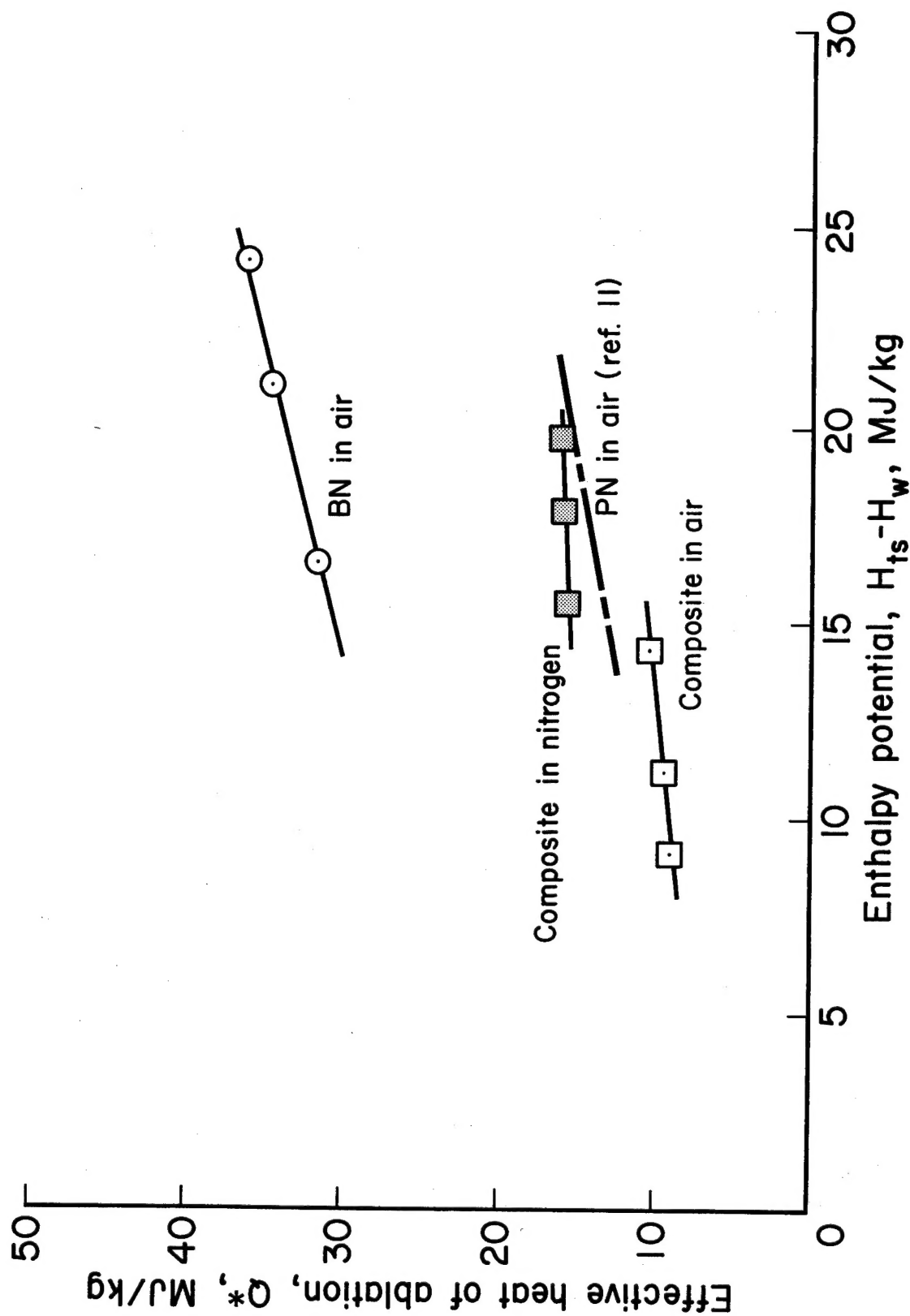


Figure 10.- Effective heat of ablation of hot-pressed boron nitride and boron nitride-phenolic resin composite.

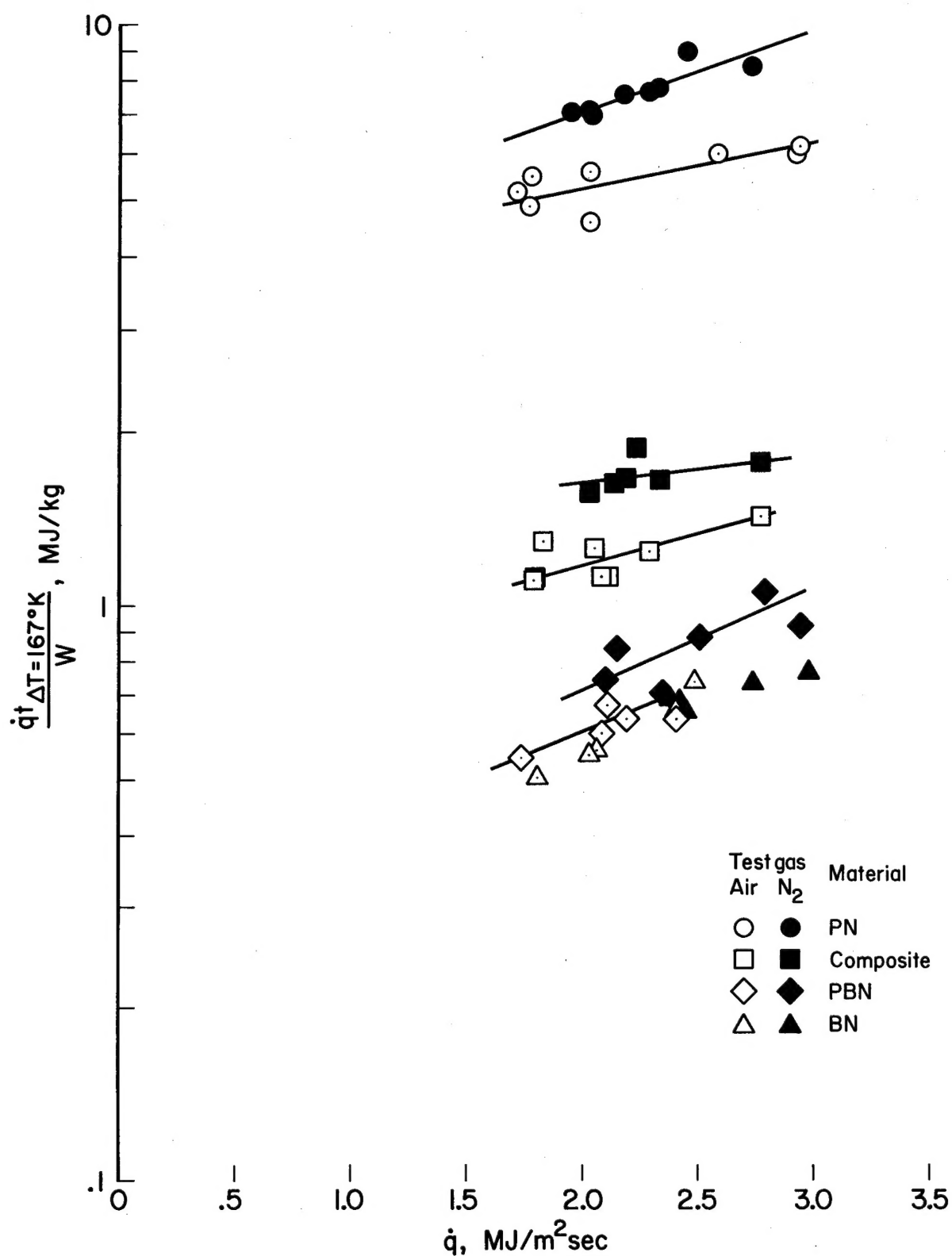


Figure 11.- Variation of insulation efficiency heating rate.

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